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Production of hybrid gels from polysorbate and gellan gum

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ABSTRACT

The association of gellan gum and nonionic surfactant in the gel formation was explored in systems with high biopolymer concentration (3% w/w). Gels formed with different concentrations of polysorbate 80 (0–60% w/v) and pH (3.0 and 5.0) were evaluated from their microstructure, mechanical and rheological properties. The high concentration of polysaccharide in water at more acidic pH (3.0) favored the aggregation of molecules, producing harder gels even at high temperatures. The thermal rheological measurements showed two distinct behaviors which depending on the predominance of polysaccharide or surfactant in the systems. The gellan gum properties were predominant at lower surfactant concentrations. However, the surfactant micelles could enhance the linkage between the macromolecules through the few remaining hydrophobic sites of the biopolymer and consequently increase the gel strength that presented strain-hardening behavior. As the surfactant concentration was increased to 30% (w/w), different slopes in the rheological curves were observed. They were attributed to the structuration of the polysorbate. At higher concentration of polysorbate, the surfactant prevented the gellan gum aggregation and the gum did not exert influence on the rheological behavior, which was related to the surfactant structuration. The surfactant self-assembly produced weaker gel-like structures than the gellan network, presenting a strain-weakening behavior. Thus, results suggest that depending on the medium conditions, gellan-polysorbate 80 interaction could produce different gels with different technological properties.

1. Introduction

Self-assembly systems have attracted the interest of different industrial segments and research lines due its versatility in relation to their structure and functionality. The surfactant molecules have the ability to self-assemble into a large variety of morphologies, including different kinds of micelles, vesicles and flexible bilayers. At high concentrations, they can spontaneously form a large variety of highly organized mesophases, as cubic, hexagonal and lamellar structures (Binks, Fletcher, & Tian, 2010; Trickett & Eastoe, 2008). Moreover, these surfactant-based systems could act as delivery vehicles of hydrophobic and hydrophilic bioactive compounds, due to the amphiphilic character of surfactant moieties (Qian, Decker, Xiao, & McClements, 2012; Rees & Robinson, 1993; Testard & Zemb, 2002). The surfactant can be classified as cationic, anionic, zwitterionic or nonionic depending on the hydrophilic head. Aiming its application in pharmaceutical and food systems, the use of nonionic surfactants is more appropriate due to the higher toxicity of ionic surfactants (Guo & Guo, 2010). Polysorbates are nonionic surfactants widely used in food products. They are derived from PEG-ylated sorbitan (hydrophilic group) esterified with fatty acids (hydrophobic group), with a total of 20 ethylene oxide subunits per molecule. The hydrocarbon chains provide the hydrophobic character of the polysorbates, while their hydrophilic nature is provided by the ethylene oxide (Jiao, 2008; Kerwin, 2008; Picone & Cunha, 2013; Yaghmur, Aserin, & Garti, 2002). The structure of the polysorbates can vary according to the length of the polyoxyethylene chain, type of fatty acid and degree of esterification, which exert influence on the self-assembly mechanisms (Petersen & Ulrich, 2011). On the other hand, the polysorbate 20 and 80 behavior in aqueous systems was reported with the formation of micellar systems and liquid crystalline with gel-like structures (Picone & Cunha, 2013).

Besides the influence of different structural arrangement among the polysorbates, external factors can affect the surfactant behavior in solution as temperature, pH, pressure and the presence of additives, as biopolymers (Fan, Liu, Xi, & Guo, 2011; Lawrence, 1994; Picone & Cunha, 2013; Tomasic, Tomasic, Smit, & Filipovic-Vincekovic, 2005). Moreover, the interaction between surfactant and biopolymers is dependent of the bulk variables (concentration, molar ratio, ionic strength, temperature, etc.) (Barreiro-Iglesias, Alvarez-Lorenzo, & Concheiro, 2003; Tomasic et al., 2005). The intrinsic characteristic of surfactant and polyelectrolyte also influence this ability (Barreiro-Iglesias et al., 2003; Goddard, 2002; Pepic, Filipovic-Grcic, & Jalsenjak, 2009).

Gellan gum is a linear extracellular polysaccharide produced by the bacteria *Sphingomonas elodea*, and composed of repeating tetrasaccharide (1,3-β-D-glucose, 1,4-β-D-glucuronic acid, 1,4-β-D-glucose, 1,4-α-L-rhamnose) units containing one carboxyl side group. Gellan gum presents gelling properties, forming hard and translucent gels, which are resistant at low pH values, differing of other food hydrocolloids as

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agar and carrageenan. These gelling properties are dependent on the ionic strength, presence and type of cations, pH, temperature and polymer concentration during its gelation (Moritaka, Nishinari, Taki, & Fukuba, 1995; Picone & Cunha, 2011; Yamamoto & Cunha, 2007). Despite the promising gelling properties of gellan gum, its interaction with surfactants has not been reported until now. However, most of these works use ionic surfactants that generally present a toxicity degree in comparison to nonionic (Guo & Guo, 2010). Moreover, a small range of surfactant and/or polysaccharide concentration was studied focusing on the chemical interaction between the components. They evaluate the effect of the biopolymer on the surfactant CMC, which means that they work in low or very low concentration. The high concentration of biopolymer and/or polysorbate could lead to different physicochemical properties that could be exploited not only by the food industry, but also by the cosmetic and pharmaceutical as oral or topical vehicles. Thus, the aim of this work was to evaluate the gellan–surfactant interactions using concentrated polysaccharide solution (3.0% w/w). The influence of surfactant concentration and pH in the systems arrangement was evaluated from their microstructure, mechanical properties and thermal rheological behavior of the gels.

2. Material and methods

2.1. Material

Deacylated gellan gum powder (Kelcogel® F) was kindly donated by Kelco Biopolymers (San Diego, CA). The surfactant polyoxyethylene sorbitan monooleate (Tween 80) was purchased from Sigma-Aldrich Co. (EUA). The acetic acid 99% (Synth, Brazil) and other reactives were of analytical grade.

2.2. Gel preparation

Gelled systems with different Tween80 concentrations (0–60% w/v) were produced in the presence or absence of 0.1 M acetic acid in order to evaluate the effect of pH in surfactant–polysaccharide interactions. Firstly, Tween80 at different concentrations was added to 100 mL of deionized water. The solutions were heated at 80 °C before the addition of gellan powder (3.0% w/w) in a jacketed vessel to facilitate the polysaccharide solubilization. The solution was maintained at 80 °C during 30 min under constant stirring to solubilize the gum. The rheological measurements were carried immediately after the heat treatment, to avoid previous gelling of the gum. For the analyses of the mechanical properties and microstructure, the mixtures were poured into cylindrical plastic tubes (21 mm inner diameter × 21 mm height) and Petri dishes, respectively, before to be cooled to 10 °C. The gels were maintained at 10 °C for 48 h in order to ensure complete gel formation.

2.3. Zeta potential

Zeta potential of gellan gum was measured in a Zetasizer Nano-ZS (Malvern Instruments, Herrenberg, Germany) with a detection angle of 173°, equipped with a MPT-2 Autotitrator (Malvern Instruments, Herrenberg, Germany). The zeta potential of 0.1% (w/v) of gellan gum at different pH was determined using titration curves from pH 3.0 to 7.0 by adding 0.25 M NaOH or 0.25 M HCl. The measurements were carried out at 25 °C in triplicate.

2.4. Electrical conductivity measurements

The electrical conductivity (κ) was determined at 80 °C before gellan addition in order to characterize the surfactant arrangement. The measurements were carried out at different pH (3.0 and 5.0) using a bench top conductivimeter Orion 3 Star (Thermo Electron Co., USA) coupled to a conductivity cell (Orion 013016MD).

2.5. Mechanical properties

Mechanical properties were determined by uniaxial compression measurements using a TA-XT Plus Texture Analyzer (Stable Micro Systems, Godalming, UK) with a cylindrical acrylic plate (60 mm diameter) lubricated with silicon oil to minimize friction between the sample and the probe. Compression was carried out at a sample temperature (10 °C) with a crosshead speed of 1 mm/s up to 80% of the original sample height. Hencky stress (σ_H) and strain (ε_H) were calculated from the force-deformation data according to Eqs. (1) and (2) (Steffe, 1996), respectively.

$$\sigma_H = F(t)\left[\frac{H(t)}{H_0 A_0}\right] \tag{1}$$

$$\varepsilon_H = -\ln\left[\frac{H(t)}{H_0}\right] \tag{2}$$

where $F(t)$ is the force (N) at time t, A_0 (m^2) and H_0 (m) are the initial area and height of the sample, respectively, and $H(t)$ is the height (m) at time t. The stress (σ_R) and strain (ε_R) at rupture were calculated considering the rupture point as the maximum point of the stress–strain curve. The stress–strain data before the rupture point was fitted to the BST equation (Blatz, Sharda, & Tschoegl, 1974), which assumes a relationship between deformation energy and radial deformation under compression that deviates from the ideal Hookean behavior (Eqs. (3) and (4)).

$$\sigma = \frac{2E_{BST}}{3\eta}\left(\lambda^{\eta} - \lambda^{-2\eta}\right) \tag{3}$$

$$\lambda = \frac{R_t}{R_0} \tag{4}$$

where λ is the radial deformation (dimensionless), R_0 is the initial sample radius (m), R_t is the radial deformation (m) at t (s) and E_{BST} is the elasticity modulus (Pa) predicted by the model. The parameter η (dimensionless) is an empirical measure of deviation from the ideal behavior where $\eta = 2$ corresponds to an ideal rubber elasticity sample, η values higher than two characterize the so-called strain-hardening behavior and η values lower than two corresponding to strain-weakening samples. Five gels of each system were analyzed.

2.6. Rheological measurements

The thermal behavior of the samples was evaluated by oscillatory shear measurements in a strain-controlled rheometer Physica MCR301 (Anton Paar, Austria) equipped with a stainless steel cone-plate geometry (50 mm, 2° angle, truncation 208 μm). The samples were transferred onto the rheometer plate (which was preheated at 80 °C) immediately after the heat treatment. A solvent trap accessory was coupled around the geometry in order to avoid sample evaporation. Cooling sweeps were carried out from 70 °C to 5 °C at 1 °C/min, using 0.1 Hz and 1% strain to ensure the viscoelastic linear region of the samples. The contribution of the elastic and viscous characteristics was evaluated from storage (G') and loss (G'') moduli. Changes in the slope of complex viscosity vs. temperature curves were maximized from the derivation of the data using the Savitzky & Golay filter (Savitzky & Golay, 1964). The transition temperature or gel point was considered significant when the slope of log (η^*) was higher than 0.1.

2.7. Scanning electron microscopy

Pieces of gel (approximately 10 mm × 2 mm × 2 mm) were fixed overnight in 2.5% glutaraldehyde in cacodylate buffer (0.1 M) at pH 7.2. After rinsing in cacodylate buffer (0.1 M), the samples were

fractured in liquid nitrogen, followed by another rinse with cacodylate buffer. The fractured samples were post-fixed overnight in 1% buffered osmium tetroxide and then dehydrated in a graded ethanolic series (30, 50, 70, 90 and 100% v/v). In order to avoid structural damage, the samples were dried at CO_2 critical point (Balzers Critical Point Dryer CPD03) and then mounted on aluminum stubs and coated with gold in a SCD 050-Balzer Sputter Coater. At least three images of typical structures were recorded at a magnification of 1.000× using JEOL JSM 5800 LV (Tokyo, Japan) microscope operating at 10 kV.

3. Results

3.1. Zeta potential

Fig. 1 shows that gellan gum was negatively charged from pH 3.0 to 7.0. The value was nearly constant around −40 mV between pH 4.0 and 7.0, but at pH 3.5 the charge density showed a pronounced increase. This result is in agreement with the study of de Jong and van de Velde (2007) that showed that the pKa of this polysaccharide is around 3.5. At pH 3.0 the zeta potential value was close to −25 mV.

3.2. Conductivity measurements

The electrical conductivity of the systems containing surfactant + water is showed in Fig. 2. The results showed that the conductivity values (κ) tended to vary with the water concentration according to a percolative conductivity profile (Mehta, Kaur, & Bhasin, 2007). At lower water content the systems are formed by discrete reverse micelles that did not interact with themselves, not contributing to the electrical conductivity. With the water fraction increase these droplets could interact and form channels leading to the increase of the κ values. Structural changes could occur and liquid crystalline systems may be formed with the surfactant decrease, increasing the values of κ up to a maximum point. After this point, at lower surfactant content, the conductivity values decrease, characterizing normal micellar systems (Mehta et al., 2007).

Despite the nonionic character of Tween80, the electrical conductivity results showed that acidification at pH 3.0 affected the self-assembly of the systems. The acid acetic pKa is around 4.8, which means that only a small fraction of this acid is ionized at pH 3.0. The neutral form of the acid may be dispersed into the surfactant phase, increasing the flexibility of the surfactant on the water interface and changing the ability of entrapped water to the structure formation (Cid-Samamed et al., 2008). Fig. 2 shows that at pH 5.0 the maximum value of κ occurred around 30–40% (w/v) of Tween80, while at more acidic pH the inversion to "normal systems" (water as continuous medium) happened at 10–20% (w/v) of surfactant.

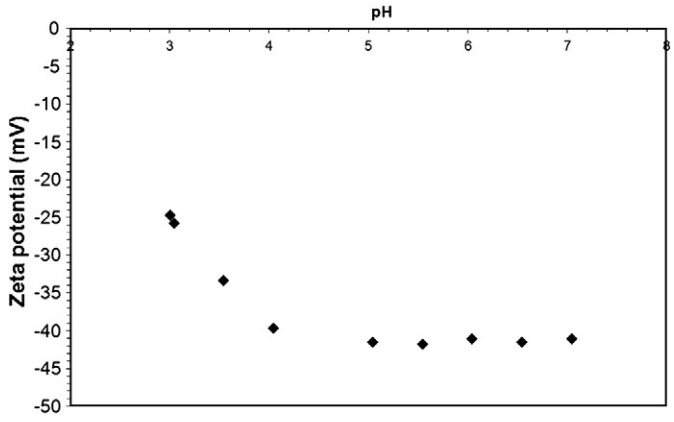

Fig. 1. Zeta potential profile of gellan gum in different pH values.

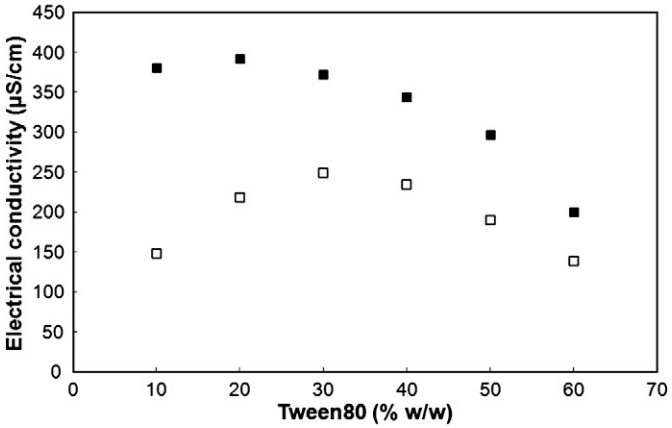

Fig. 2. Electrical conductivity (κ) of Tween80/water systems at 80 °C. (■) pH 3.0, and (□) pH 5.0.

3.3. Scanning electron microscopy (SEM)

Micrographs of typical gellan gel structures (Fig. 3), showed a porous network (de Jong & van de Velde, 2007; Picone & Cunha, 2011). The addition of surfactant apparently did not change the gel network (Fig. 3B). However, at pH 3.0 the network presented more compact structures with smaller pores even in the presence of surfactant (Fig. 3C). Systems with high Tween80 concentration (>30% w/v) could not be subjected to SEM, since the gel dissolved in the buffers during the preparation of the samples.

3.4. Oscillatory measurements

The thermal rheological behavior of the systems during cooling is shown in Fig. 4. Gelation of gellan solutions (3.0% w/w) at natural pH (pH 5.0) and in the absence of Tween80 (Fig. 4A) shows that the system was predominantly viscous at the beginning of cooling, showing higher values of G'' than G'. However, the elastic modulus became higher than G'' with temperature decrease, which is characteristic of gel formation. Table 1 shows the crossover temperature or gelling point for gellan gum at natural pH, which was around 56 °C. However, Miyoshi, Takaya, and Nishinari (1996) reported a transition temperature around 40 °C for 3.0% gellan gum solution. Such difference could be attributed to the different degree of acylation and mineral composition of the gellan gum used, which could change the ionic strength of the gum and consequently its conformational transition. On the other hand, crossover was not observed and storage modulus was higher than G'' within the temperature range evaluated in more acidic condition (pH 3.0).

With the surfactant addition two different transitions were observed and could be related to gellan or polysorbate effect depending on the concentration of these components. At lower concentrations (10–30% w/w) of Tween80 the predominant behavior was attributed to the polysaccharide, with one or none gel point depending on the pH. The storage and loss moduli became closer with the surfactant addition, but the difference between G' and G'' was higher for system at more acid pH. The moduli values did not show strong differences at 10 °C for all surfactant concentrations, but at 70 °C these values started to decrease with Tween80 higher than 30% (w/w) (Fig. 4D). At this surfactant, concentration of the rheological profile of both pH studied did not show a significant change in the complex viscosity that could characterize a specific gel point (Table 1). At 40% (w/v) of surfactant a transition behavior was observed and two different slopes could be observed (Fig. 4E and Table 1). The slope at lower temperatures (between 52 and 56 °C for pH 5.0) could be attributed to the surfactant self-assembly (Picone & Cunha, 2013), which forms more complex structures at lower temperatures (Venugopal, Bhat, Vallooran, & Mezzenga,

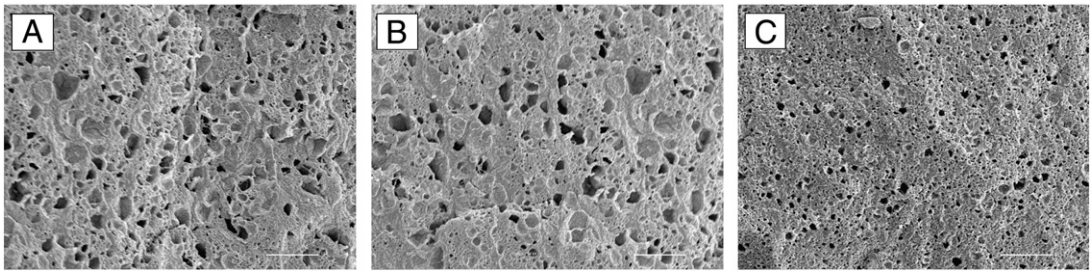

Fig. 3. SEM micrographs of 3.0% (w/w) gellan gum gels. (A) Natural pH (5.0) and 0% of Tween80; (B) natural pH and 10% of Tween80 and (C) pH 3.0 and 10% of Tween80.

2011; Wadsten-Hindrichsen, Bender, Unga, & Engstrom, 2007). The prevailing behavior that clearly changed at 50% (w/v) of Tween80 could be attributed to the polysorbate structuration. Moreover, the pH did not exert influence, since this surfactant was nonionic. In both pH conditions, the rheograms showed a slope change close to 45 °C (Table 1) and such temperature decreased with the increase of surfactant concentration, as previously observed by Picone and Cunha (2013). Moreover, at these concentrations the surfactant was able to form complex gel-like structures, but these were weaker in comparison to those formed with only gellan.

3.5. Mechanical properties

Fig. 5 shows typical stress–strain curves obtained from the uniaxial compression measurements. Overall, two different tendencies were observed. The curve (A) represents a harder gel that presented a clear rupture point. Curve (B) shows the behavior of a squeezing gel, which means that such gel did not show a rupture point but it flowed with the force application presenting a maximum or squeezing stress. It was observed that the surfactant influenced mechanical properties depending on its concentration and system pH. From 40% (w/v) of Tween80 the gels were smashed, showing no rupture point (Fig. 6). Harder (maximum stress at rupture — σ_{max}) or less deformable (lower strain at rupture — ε_{max}) gels were obtained in the absence or low concentration (<20% w/v) of Tween80 and lower pH value (Fig. 6). On the other hand, the values of the maximum stress (σ_{max}) decreased with the surfactant concentration increasing, especially for the acid systems, followed by an increase in the deformability (ε_{max}) of the gels.

The linear region is limited to the range where the applied stress causes no damage to the gel structure and the strain is totally reversible. Such behavior can be evaluated from the elastic modulus (E). Moreover, the BST fitting (η values) can characterize the nonlinear region of the stress–strain curves besides of the maximum stress and strain. The BST parameters (Table 2) showed that the gel formed behaved as strain-hardening ($\eta > 2$) or strain weakening ($\eta < 2$) depending on the Tween80 concentration. The addition of surfactant increased this parameter up to 20% (w/v) of surfactant content, decreasing from 30% of polysorbate. Moreover, the system became softer with 50% (w/v) of surfactant and a squeezing gel was formed with strain-weakening behavior. In relation to the elastic modulus (E_{BST}) no tendency was clearly observed and other authors observed that the BST model was not a good predictor of the elasticity modulus parameters for harder gels (Picone, Maximo, Kuhn, Ros-Polski, & Cunha, 2011; Valim, Cavallieri, & Cunha, 2009).

4. Discussion

The gelation mechanism of gellan gum is related to its conformational coil–helix transition. At high temperatures this polysaccharide is in coil conformation, and with cooling the transition occurs followed by the association between the helices, resulting in the network formation (Milas & Rinaudo, 1996). Coil–helix transition is independent of the solution pH, but the helix–coil transition was observed only at pH higher than 3.5 (Fig. 4A). This behavior could be related to the lower electrostatic repulsion at acid pH (Fig. 1) that could improve the aggregation of the biopolymer (Yamamoto & Cunha, 2007) with a strong network formation even at high temperatures. Such network can be observed in the micrographs (Fig. 3) and its strength could be evaluated from the enhanced mechanical properties. The denser network was able to distribute more homogeneously the force applied, showing gels with higher stress at rupture or hardness. In addition, gels at low pH presented low deformability (Fig. 6) and a strain-hardening behavior (Table 2). However, with polysorbate addition the gelation behavior changed and the surfactant–polysaccharide interaction was dependent of the pH and Tween80 concentration, resulting in different physical properties of gels.

At lower surfactant concentration (10% w/v) the SEM results (Fig. 3) showed that the Tween80 addition did not change the gel structure, which means that its properties were more dependent on the gellan–gellan interactions. However, the rheological behavior was quite similar at both pH, which means that the surfactant presence strongly modified the gelation properties at gellan natural pH (Fig. 4B and Table 1). The surfactant concentration used in these systems was much greater than the critical micelle concentration (CMC). Therefore, at this concentration, the surfactant moieties could be aggregated in the micellar form, which could occupy the pores formed by the gellan gum network. According to the electrical conductivity (Fig. 2), the surfactant was self-assembled in “normal structures” with the hydrophobic tails in the core of the structure and the hydrophilic head driven to the water medium. Since the deacylated gellan gum was used, few hydrophobic groups remained linked to its hydrophilic backbone. Nevertheless, these groups could have linked to the hydrophobic tails of the polysorbate creating a crosslink effect. This arrangement was previously reported as a necklace with surfactant pearls (Grant, Cho, & Allen, 2006; Tsianou & Alexandridis, 2004). However, such arrangement changed the rheological behavior of gellan pure systems (Fig. 4) preventing the strong aggregation of the polysaccharide macromolecule that showed a decrease of the storage modulus (G'). Moreover, the decrease in the water content make the gellan solution more concentrated. The network formed by this more concentrated solution offered more resistance to the normal forces applied, which could explain the small increase in the stress at rupture (Fig. 6). Such behavior (necklace with surfactant pearls), was also observed with the addition of 20% (w/w) and natural pH, but at more acidic pH softer gels with lower stress at rupture were produced. Electrical conductivity measurements (Fig. 2) indicated that at pH 3.0 the surfactant could be more organized or starting to form reverse structures. The surfactant molecules present high mobility in comparison to the biopolymer. The self-assembly of the polysorbate in organized structures is more dynamic, occurring in a quickly time scale (1 μs) compared to the kinetics of polymerization or gelling process (1 ms) (Magno, Tessendorf, Medronho, Miguel, & Stubenrauch, 2009). Thus, this surfactant self-assembly in reverse structures caused a steric effect, preventing the polysaccharide aggregation and consequently forming not as harder gels.

At 30% (w/w) both systems already crossed by the maximal electrical conductivity values (Fig. 2), which means that reverse structures

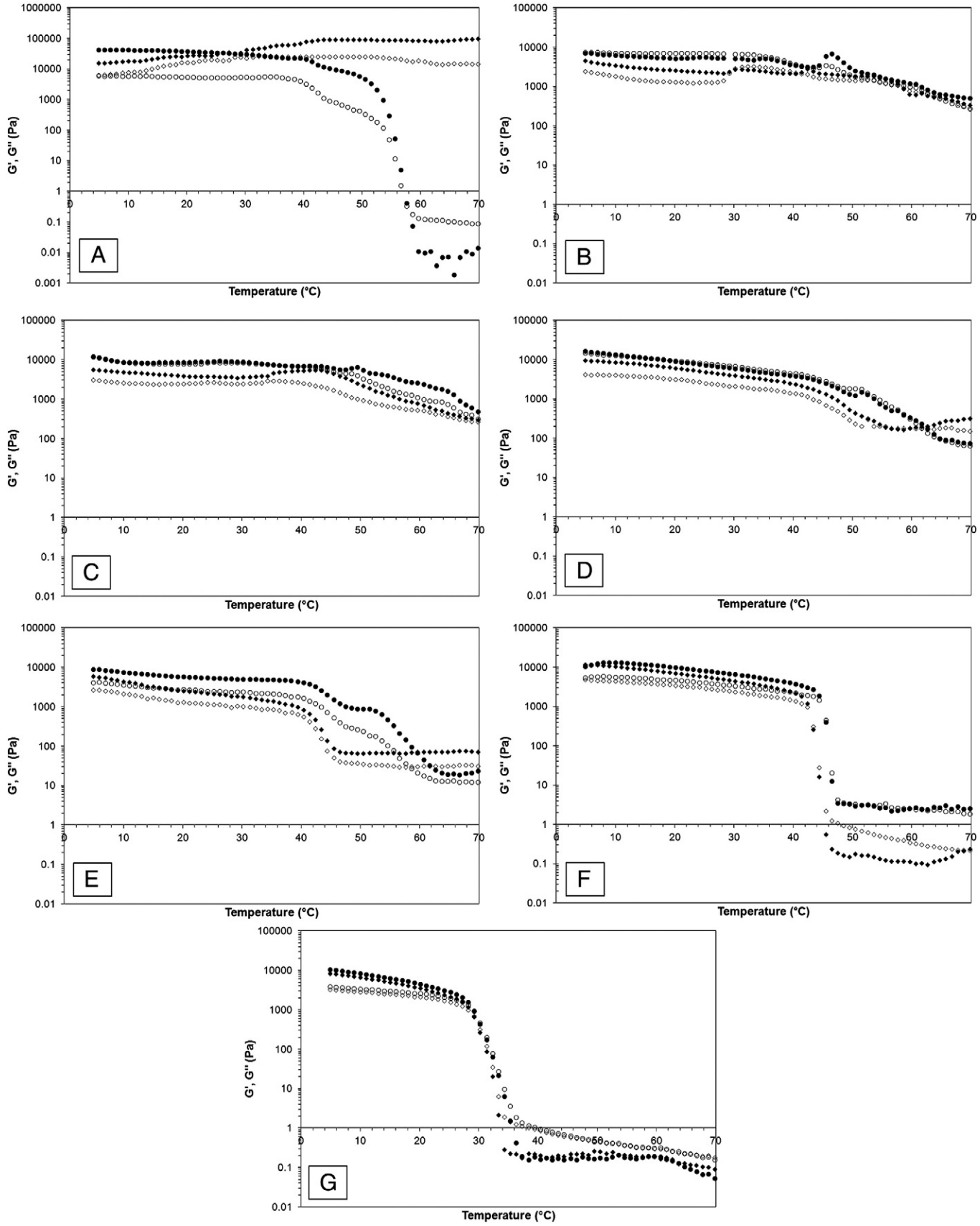

Fig. 4. Thermal scanning rheograms of gels with 3.0% (w/w) gellan gum at natural pH (5.0) and pH 3.0 containing different concentrations of Tween80. (A) 0%; (B) 10%; (C) 20%; (D), 30%; (E), 40%, (F) 50% and (G) 60%. (♦,◊) pH 3.0 and (●,○) pH 5.0 (natural). Full and empty symbols refers to G′ and G″, respectively.

Table 1
Gel or transition temperatures for systems with 3.0% (w/w) gellan gum at natural pH (5.0) or pH 3.0 with different Tween80 concentration.

pH	Tween80 (%)	Transition temperatures (°C)	
		Surfactant structuration	Polysaccharide gelling
3.0	0	–	>70
	10	–	>70
	20	–	>70
	30	53 ± 2.3	>70
	40	47 ± 0.5	>70
	50	44 ± 0.7	–
	60	35 ± 2.1	–
5.0	0	–	56 ± 2.5
	10	–	64 ± 0.7
	20	–	66 ± 1.8
	30	57 ± 1.0	66 ± 0.2
	40	48 ± 1.1	59 ± 0.7
	50	47 ± 3.1	–
	60	36 ± 0.5	–

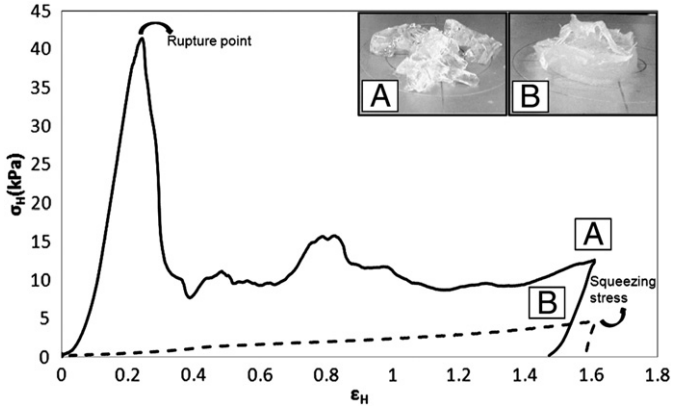

Fig. 5. Typical uniaxial compression curves for 3.0% (w/w) gellan gum gels. (A) Gel with rupture point and (B) squeezing gel.

were formed. The mechanical properties were similar for gels at natural and more acidic pH. Still, two slopes were observed in the thermal rheological behavior (Fig. 4C and Table 1), one associated to gellan gelation and the other could be related to the surfactant structuration. Depending on the concentration of the surfactant and its physical characteristics, the molecular self-assembly can occur assuming a large variety of morphologies denominated as liquid crystalline phase (Binks et al., 2010). The liquid crystalline systems present high viscosity or even gel-like structures depending on the moiety organization (Lawrence, 1994; Rehage, 2005).

Above this concentration, the surfactant properties were predominant in both pH, but with some influence of gellan network. At 40% (w/v) of Tween80 two distinct behaviors were observed during gel formation. At natural pH the interaction mechanism was the same as observed at 30% (w/w) of surfactant content. The surfactant was still not able to form gel-like structure; despite that, there were some linkages between gellan gum macromolecules, conferring the strain-hardening behavior (Table 2) for the squeezing gel formed. On the other hand, at pH 3.0 non-self supportable gel was obtained. The reverse surfactant structure and the higher aggregation degree of the gellan gum at this pH prevented the formation of a network leading to separated aggregates and the system showed a granulated (particulate) appearance. At 50% and 60% (w/w) of Tween80 only the slope related to the surfactant structuration was observed in the rheological curves (Fig. 4F–G). Such Tween80 structuration depending on temperature was previously reported (Picone & Cunha, 2013), showing that between 50 and 70% (w/w), this surfactant presents a gel-point. The crossover temperature decreased from 45 °C to 37 °C at 50 and 60% (w/w), respectively with surfactant concentration increase. Such behavior was also observed in our results but the structuration temperature was 45 °C and 30 °C at 50 and 60% (w/w) of surfactant, respectively in the presence of gellan (Table 1). Moreover, the high surfactant concentration prevented the interactions between gellan gum molecules (Holmberg, Jönsson, Kronberg, & Lindman, 2002; Tsianou & Alexandridis, 2004) and decreased the storage moduli. At last, the surfactant based gels with predominance of surfactant properties did not present rupture point (Fig. 6), showing a strain-weakening behavior (Table 2).

5. Conclusion

The conformational arrangement of gellan gum and the self-assembly of polysorbate 80 led to gelled structures with different behaviors, which were dependent on the surfactant concentration and pH. The high concentration of gellan gum formed gels depending on the pH. At natural pH, the gel point temperature of pure gellan gels was high, nevertheless, at acidic pH the system showed harder gels with elastic behavior independent of the temperature. The gellan gum properties prevailed up to 20% of surfactant. Even so, at this polysorbate concentration range, the surfactant micelles prevented the gellan–gellan interactions changing the sample rheological behavior. Surfactant increase transition systems were observed with two temperature transitions that could be related to the polysaccharide gelation and surfactant structuration. At higher Tween80 concentrations (50–60% w/v) the surfactant self-assembled in gel-like liquid crystalline structures with prevailing behavior of the polysorbate80. Thus, depending on the conditions of the systems, the physical properties of the gelled systems could present predominant behavior relative to gellan or surfactant. Moreover, gellan-polysorbate80 interactions could produce harder or softer gels with different technological characteristics. These differences could allow the application of these gels in products with different aims,

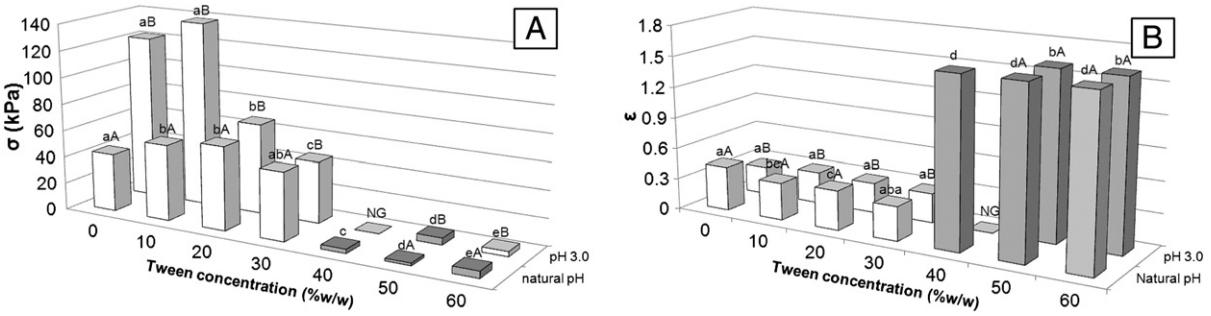

Fig. 6. Mechanical properties of gels of 3.0% (w/w) gellan gum at natural pH and pH 3.0 with different Tween80 concentration. (A) Maximum stress (σ) and (B) strain (ε). White bars refer to gels with rupture point and gray bars to squeeze gels. Means with different letters show statistically significant differences ($p < 0.05$): Capital letters on the z axis and small letter on the x axis. NG — non-self supporting gels.

Table 2
BST parameters of gels of 3.0% (w/w) gellan gum at natural pH and pH 3.0 with different Tween80 concentration.

pH	Tween80 (%)	BST parameters		
		E_{BST} (kPa)	H	R^2
3.0	0	3.1 ± 0.32	12.2 ± 0.7	0.98
	10	1.2 ± 0.1	16.6 ± 0.6	0.97
	20	92.4 ± 23.2	39.2 ± 4.3	0.99
	30	33.3 ± 1.0	30.3 ± 3.8	0.99
	40	NG	NG	–
	50	6.8 ± 0.5	0.8 ± 0.01	0.90
	60	6.7 ± 0.34	1.4 ± 0.1	0.91
5.0	0	85.1 ± 3.6	18.9 ± 0.4	0.90
	10	139 ± 38.4	20.1 ± 1.7	0.91
	20	63.2 ± 6.2	32.4 ± 4.8	0.99
	30	44.2 ± 7.3	31.8 ± 1.7	0.99
	40	11.2 ± 1.5	8.1 ± 0.6	0.99
	50	2.7 ± 0.06	1.2 ± 0.03	0.92
	60	4.2 ± 0.41	0.8 ± 0.02	0.96

*NG — non-self supporting gels.

as texture modifiers or even vehicle for bioactives in food, pharmaceutical or cosmetic industries.

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